

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 February 2002 (14.02.2002)

PCT

(10) International Publication Number
WO 02/12616 A1

(51) International Patent Classification⁷: **D06M 13/425**,
23/04, D06L 1/04, D01F 11/06

(21) International Application Number: **PCT/EP01/08662**

(22) International Filing Date: **26 July 2001 (26.07.2001)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
00810702.1 **4 August 2000 (04.08.2000)** **EP**

(71) Applicant (*for all designated States except US*): **CIBA
SPECIALTY CHEMICALS HOLDING INC. [CH/CH];**
Klybeckstrasse 141, CH-4057 Basel (CH).

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **MAO, Jianwen**
[CN/DE]; Ruschbachstrasse 29, 79639 Grenzach-Wyhlen
(DE).

(74) Agent: **CIBA SPECIALTY CHEMICALS HOLDING,
INC.;** Patentabteilung, Klybeckstrasse 141, CH-4057
Basel (CH).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK,
SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA,
ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SI, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD,
TG).

Published:

- *with international search report*
- *before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments*

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: A METHOD FOR THE TREATMENT OF TEXTILE MATERIALS AGAINST FUNGI AND DUST MITES

(57) Abstract: Described is a method of use for the treatment of textile material to improve the antifungal and/or antidustmite properties, comprising applying to the textile material a compound of formula by padding, spraying, foam application or during a dry cleaning processor and a similar process related to the treatment of polyacrylonitrile fibres in the gel state.

WO 02/12616 A1

A METHOD FOR THE TREATMENT OF TEXTILE MATERIALS AGAINST FUNGI AND DUST MITES

A method of use for the treatment of textile materials

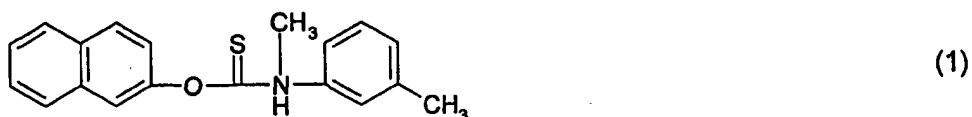
The present invention is directed to a method of use for the treatment of textile materials to improve the antifungal and/or antidustmite properties by applying to the textile materials a special selected antifungal or antidustmite agent by special application processes.

Textile products that exhibit antifungal properties, especially those that exhibit antidustmites properties are highly desirable by the consumers. A few segments are of particular importance for such properties. For example, various studies have found that human feet are often infected with fungi resulting in various diseases such as Athlete's foot. Textile materials that exhibit antifungal properties and when incorporated as components for making shoes, could therefore be beneficial to consumers. In home textile segment, dustmites present in matrices, pillow cases have been linked to the increasing occurrence of allergy and asthma. Since the survival of dustmites are dependent on the presence of fungal species to metabolise the skin flaks to provide Vitamin B, a vital food source for the dustmites, the inhibition of fungal would help prevent the growth of dustmites, therefore bring benefits to the consumers.

In view of the above there is a need to find a suitable process that allows to improve these properties and according to which long lasting antifungal and antidustmite activities are obtained which are also durable against repeated laundering.

The present invention is focused on the use of a special agent in textile products to provide the desirable antifungal and antidustmite efficacy. Surprisingly it was found that a selected antifungal substance can be incorporated onto various substrates made of man made as well as natural fibres to provide long lasting antifungal activities and antindustmite properties that are durable against repeated laundering, dry cleaning, weathering and/or other ageing processes. It was found that the treatment of such textile products with a selected agent and/or formulations that contain such an agent could be carried out in various processes such as padding, spraying and foam application processes as well as processes wherein polyacrylonitrile fibres are treated with the agent in the gel state.

The present invention, therefore, relates to a method of use for the treatment of textile material to improve the antifungal and/or antidustmite properties, comprising applying to the textile material a compound of formula



by padding, spraying, foam application or during a dry cleaning process.

The compound of formula (1) may be applied as aqueous formulation in diluted, solubilised, emulsified or, preferably, in dispersed form.

Such aqueous formulations therefore can additionally comprise a small amount of an organic solvent, a surfactant, a dispersant, and/or an emulsifier. These components are useful for solubilisation and stabilisation of the compound of formula (1) in the aqueous formulation.

If the compound of formula (1) is applied in dispersed form it is preferably milled with an appropriate dispersant, conveniently using quartz balls and an impeller, for example to a particle size of 0.1 to 4 μm , especially 0.3 to 3 μm .

Suitable dispersants for the compound of formula (1) are:

- acid esters or their salts of alkylene oxide adducts, typically acid esters or their salts of a polyadduct of 4 to 40mol of ethylene oxide with 1mol of a phenol, or phosphated polyadducts of 6 to 30mol of ethylene oxide with 1mol of 4-nonylphenol, 1mol of dinonylphenol or, preferably, with 1mol of compounds which are prepared by addition of 1 to 3mol of unsubstituted or substituted styrenes to 1mol of phenol,
- polystyrene sulfonates,
- fatty acid taurides,
- alkylated diphenyl oxide mono- or disulfonates,
- sulfonates of polycarboxylates,
- the polyadducts of 1 to 60 mol of ethylene oxide and/or propylene oxide with fatty amines, fatty acids or fatty alcohols, each containing 8 to 22 carbon atoms in the alkyl chain, with alkylphenols containing 4 to 16 carbon atoms in the alkyl chain, or with trihydric to

hexahydric alkanols containing 3 to 6 carbon atoms, which polyadducts are converted into an acid ester with an organic dicarboxylic acid or with an inorganic polybasic acid,

- ligninsulfonates, and, most preferably,
- formaldehyde condensates such as condensates of ligninsulfonates and/or phenol and formaldehyde, condensates of formaldehyde with aromatic sulfonic acids, typically condensates of ditolyl ether sulfonates and formaldehyde, condensates of naphthalenesulfonic acid and/or naphthol- or naphthylaminesulfonic acids with formaldehyde, condensates of phenolsulfonic acids and/or sulfonated dihydroxydiphenylsulfone and phenols or cresols with formaldehyde and/or urea, as well as condensates of diphenyl oxide-disulfonic acid derivatives with formaldehyde.

Preferably the compound of formula (1) is dispersed with at least one dispersant selected from the group consisting of condensates of ligninsulfonates and/or phenol and formaldehyde; condensates of formaldehyde with aromatic sulfonic acids; condensates of naphthalenesulfonic acid and/or naphthol- or naphthylaminesulfonic acids with formaldehyde; condensates of phenolsulfonic acids and/or sulfonated dihydroxydiphenylsulfone and phenols or cresols with formaldehyde and/or urea; and condensates of diphenyl oxide-disulfonic acid derivatives with formaldehyde. Highly preferred are condensates of naphthalenesulfonic acid and/or naphthol- or naphthylaminesulfonic acids with formaldehyde.

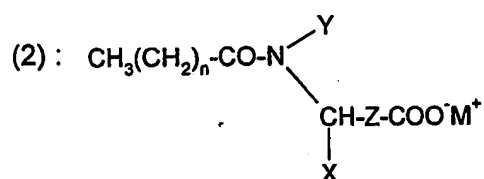
Suitable solubilising agents are anionic, nonionic or zwitterionic and amphoteric synthetic, surface-active substances.

Suitable anionic surface-active substances are:

- sulfates, typically fatty alcohol sulfates, which contain 8 to 18 carbon atoms in the alkyl chain, e.g. sulfated lauryl alcohol;
- fatty alcohol ether sulfates, typically the acid esters or the salts thereof of a polyadduct of 2 to 30 mol of ethylene oxide with 1 mol of a C_8 - C_{22} fatty alcohol;
- the alkali metal salts, ammonium salts or amine salts of C_8 - C_{20} fatty acids, which are termed soaps, typically coconut fatty acid;
- alkylamide sulfates;
- alkylamine sulfates, typically monoethanolamine lauryl sulfate;
- alkylamide ether sulfates;

- alkylaryl polyether sulfates;
- monoglyceride sulfates;
- alkane sulfonates, containing 8 to 20 carbon atoms in the alkyl chain, e.g. dodecyl sulfonate;
- alkylamide sulfonates;
- alkylaryl sulfonates;
- α -olefin sulfonates;
- sulfosuccinic acid derivatives, typically alkyl sulfosuccinates, alkyl ether sulfosuccinates or alkyl sulfosuccinamide derivatives;

N-[alkylamidoalkyl]amino acids of formula (2):



wherein

X is hydrogen, $\text{C}_1\text{-C}_4$ alkyl or $\text{-COO}^-\text{M}^+$,

Y is hydrogen or $\text{C}_1\text{-C}_4$ alkyl,

Z is: $\text{-(CH}_2\text{)}_{m_1-1}$

m_1 is 1 to 5,

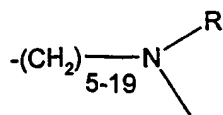
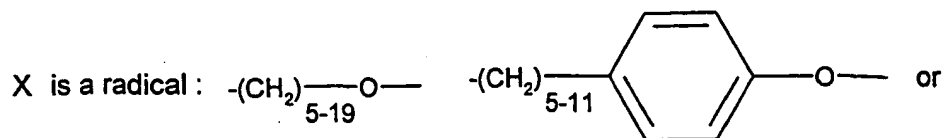
n is an integer from 6 to 18, and

M is an alkali metal ion or an amine ion;

- alkyl ether carboxylates and alkylaryl ether carboxylates of formula



wherein



R is hydrogen or C₁-C₄ alkyl,

Y is: $-(\text{CH}_2\text{CH}_2\text{O})_{1-50}-$

A is: $-(\text{CH}_2)_{m_2-1}-\text{COO}^-\text{M}^+$ or: $\begin{array}{c} \text{O} \\ \parallel \\ -\text{P}-\text{O}^-\text{M}^+ \\ | \\ \text{O}^-\text{M}^+ \end{array}$

m₂ is 1 to 6, and

M is an alkali metal cation or an amine cation.

The anionic surfactants used may furthermore be fatty acid methyl taurides, alkylisothionates, fatty acid polypeptide condensates and fatty alcohol phosphoric acid esters. The alkyl radicals in these compounds preferably contain 8 to 24 carbon atoms.

The anionic surfactants are usually obtained in the form of their water-soluble salts, such as the alkali metal, ammonium or amine salts. Typical examples of such salts are lithium, sodium, potassium, ammonium, triethylamine, ethanolamine, diethanolamine or triethanolamine salts. It is preferred to use the sodium or potassium salts or the ammonium-(NR₁R₂R₃) salts, wherein R₁, R₂ and R₃ are each independently of one another hydrogen, C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl.

Suitable zwitterionic and amphoteric surfactants are imidazoline carboxylates, alkylamphocarboxy carboxylic acids, alkylamphocarboxylic acids (e.g. lauroamphoglycinate) and N-alkyl-b-aminopropionates or N-alkyl-b-iminodipropionates.

Nonionic surfactants are typically derivatives of the adducts of propylene oxide/ethylene oxide having a molecular weight of 1000 to 15000, fatty alcohol ethoxylates (1-50 EO), alkylphenol polyglycol ethers (1-50 EO), ethoxylated carbohydrates, fatty acid glycol partial esters, typically diethylene glycol monostearate, PEG 5 glyceryl stearate; PEG 15 glyceryl stearate; PEG 25 glyceryl stearate; cetearyl octanoate; fatty acid alkanolamides and fatty acid dialkanolamides, fatty acid alkanolamide ethoxylates and fatty acid amine oxides.

Furthermore, the salts of saturated and unsaturated C₈-C₂₂ fatty acids may be used as

solubilising agents, either by themselves, in admixture with each other or in admixture with the other surface-active substances. Illustrative examples of these fatty acids are typically capric, lauric, myristic, palmitic, stearic, arachic, behenic, dodecenoic, tetradecenoic, octadecenoic, oleic, eicosanic and erucic acid, as well as the technical mixtures of such acids, typically coconut fatty acid. These acids may be obtained in the form of salts, suitable cations being alkali metal cations such as sodium and potassium cations, metal atoms such as zinc atoms and aluminium atoms or nitrogen-containing organic compounds of sufficient alkalinity, typically amines or ethoxylated amines. These salts can also be prepared in situ.

Furthermore, suitable solubilising agents are dihydric alcohols, preferably those containing 2 to 6 carbon atoms in the alkylene radical, typically ethylene glycol, 1,2- or 1,3-propanediol, 1,3-, 1,4- or 2,3-butanediol, 1,5-pentanediol and 1,6-hexanediol or monohydric alcohol like methanol, ethanol or propanol, and acetone.

In such aqueous formulations, especially in the dispersions, the concentration of the compound of formula (1) is usually 0.001% to 30% by weight, based on the weight of the formulation, especially 0.1% to 20%. Highly preferred is an amount of the compound of the formula (1) of 0.1% to 10%, especially 1% to 5%.

The amount of additionally added components, like dispersants or surfactants, is preferably 0.1% to 30% by weight, especially 1% to 20%, each amount based on the weight of the aqueous formulation.

The aqueous formulation, especially the dispersion prepared by the above method, can be diluted to almost any ratio.

For all of the following applications it is preferred to add the compound of formula (1) in form of such aqueous formulations, especially in form of dispersions.

Padding can be carried out according to conventional padding processes. For example, the textile material is passed through an aqueous liquor containing the compound of formula (1), the textile material is squeezed to a defined liquor pick-up rate and then carrying out a fixation step, preferably a heat treatment.

The amount of the compound of formula (1) in the aqueous liquor (padding liquor) is usually 0.001% to 10% by weight, especially 0.01% to 10% by weight, based on the weight of the aqueous liquor. An amount of compound of formula (1) of 0.01% to 5% by weight is preferred.

The liquor pick-up rate is usually 40% to 200% by weight, especially 50% to 150% by weight, based on the weight of the textile material.

The fixation step is usually carried out by a heat treatment, for example at a temperature of 60 to 150°C, especially 90 to 150°C.

The padding process is usually carried out as a continuous process wherein the textile material is continuously passed through the aqueous liquor containing the compound of formula (1).

According to a preferred method the compound of formula (1) is applied to the textile material by padding wherein said textile material is continuously passed through an aqueous liquor containing 0.001% to 10% by weight, based on the weight of the aqueous liquor, of the compound of formula (1).

Spraying can be carried out according to conventional spraying processes. According to these processes aqueous liquids containing the compound of formula (1) are sprayed onto the textile material. The amount of the compound of formula (1) in the aqueous liquor is usually 0.001% to 10% by weight, especially 0.01% to 10% by weight, based on the weight of the aqueous liquor. An amount of compound of formula (1) of 0.1% to 10% by weight is preferred. Such spraying processes are especially suitable for applying the compound of formula (1) to textile materials like carpets. According to such preferred processes a plurality of spray nozzles are disposed in a spray line transverse to the direction of movement of, for instance, the carpet. The compound of formula (1) is applied as an aqueous liquor by the spray nozzles, for example by virtue of pressure.

After spraying usually a fixation step is carried out which can be performed by a heat treatment as given above for the padding process.

Spraying can also be used to apply the compound of formula (1) in form of an aqueous liquor to surfaces of textile materials including leather, like sofas or shoes.

According to another preferred method the compound of formula (1) is applied to the textile material by spraying, wherein an aqueous liquor containing 0.001 to 10% by weight, based on the weight of the aqueous liquor, of the compound of formula (1) is sprayed onto the textile material.

The compound of formula (1) can also be applied to the textile material by foam application. As to this application all of the above conditions and preferences given above for the spraying process apply. However, the compound of formula (1) is applied in form of an aqueous foam which usually in addition contains a foam stabiliser. Such a process is also especially suitable for treating carpets.

According to a further preferred method the compound of formula (1) is applied to the textile material by foam application, wherein an aqueous foam containing 0.001% to 10% by weight, based on the weight of the aqueous foam, of a compound of formula (1) and optionally a foam stabiliser is applied to the textile material.

Padding, spraying or foam applications can be carried out by applying the compound of formula (1) to the textile material together with dyestuffs (for example in a dyeing process) or in other textile related processes, like finishing processes. It is preferred to carry out the treatment with the compound of formula (1) in the presence of dyestuffs.

If these processes are carried out without the presence of dyestuffs it is preferred to apply the compound of formula (1) in a finishing process.

The use of some polymeric as well as oligomeric substances that are commonly used in the textile industries, can help to further improve the durability of the desirable antifungal and antidustmites efficacy. Such substances include, but are not limited to, resin finishings that

provide easy care and /or other properties to various textile materials, softeners, coating materials, fixation agents and /or other finishing agents such as hydrophilic and hydrophobic agents, flame retardant etc. It is obvious, from economic as well as process convenience perspective, that the antimicrobial treatment could be carried out together with many other different types of treatments that are found in the textile industries.

The application of the compound of formula (1) can also be carried out in a dyeing process which is carried out by padding, spraying or foam application. For these processes the above conditions and preferences apply. Suitable dyes are disperse dyes, basic dyes, acid dyes, direct dyes or reactive dyes. Reactive dyes are especially suitable for natural polyamide- or cellulose-containing textile materials. Direct dyes are especially suitable for cellulose-containing textile materials. The dyes may belong to different dye classes, including acridone, azo, anthraquinone, coumarin, formazane, methine, perinone, naphthoquinone-imine, quinophthalone, styryl or nitro dyes. Mixtures of dyes may also be used.

When using the compound of formula (1) in a dyeing process, the procedure can be such that the textile material is first treated with this compounds and then dyeing is carried out or, preferably, the textile material is treated simultaneously with the compound of formula (1) and the dye. The application of the compound of formula (1) can, however, also be effected subsequently to the previously prepared dyeing.

The treatment liquors may also contain further ingredients such as dyeing assistants, dispersants, carriers, wool protectives, and wetting agents as well as antifoams.

The treatment liquors may also contain mineral acids, typically sulphuric acid or phosphoric acid, or conveniently organic acids, typically including aliphatic carboxylic acids such as formic acid, acetic acid, oxalic acid or citric acid and/or salts such as ammonium acetate, ammonium sulfate or sodium acetate. The acids are used in particular to adjust the pH of the liquors, for example to a pH of 3 to 6.

After the dyeing process including the application of the compound of formula (1) the textile material can be subjected to a fixation step, like a heat treatment as given above.

Besides the above application processes it is also possible to apply the compound of formula (1) according to normal exhaustion processes together with a dyestuff or without presence of dyestuffs.

The compound of formula (1) can also be applied during a dry-cleaning process. According to dry-cleaning processes typically organic solvents, especially volatile organic solvents like perchloroethylene or trichloroethylene, are used as a cleaning medium. A typical dry-cleaning process consists of a wash, rinse and drying cycle. It is preferred to use an organic solvent, which contains 0.001% to 10% by weight, based on the weight of the organic solvent, of a compound of formula (1). As to the amount of compound of formula (1) the above preferences given for the padding process apply.

According to a preferred embodiment the compound of formula (1) is applied to the textile material during a dry-cleaning process, wherein the textile material is treated with an organic solvent, preferably perchloroethylene or trichloroethylene, containing 0.001% to 10% by weight, based on the weight of the organic solvent, of a compound of formula (1).

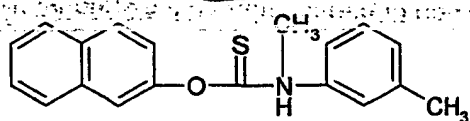
Textile materials which can be treated with the compound of formula (1) are materials comprising, for example, natural or synthetic polyamide (like wool, silk, nylon), polyurethane, polyester, polypropylene, polyethylene, polyacrylonitrile and cellulose-containing textile materials of all kinds, for example natural cellulose fibres, such as cotton, linen, jute and hemp, and also viscose staple fibre and regenerated cellulose; or blends of the above fibre materials, like polyacrylonitrile/polyester, polyamide/polyester, polyester/cotton, polyester/viscose and polyester/wool.

Preferred textile materials are those comprising wool, synthetic polyamide, polyester, polypropylene, polyethylene, and cellulose-containing textile materials, preferably cotton or wool and especially cotton.

The textile material can be in different forms of presentation, as woven or knitted fabrics or as piece goods such as knitgoods, nonwoven textiles, carpets, yarn or staple fibres. Preferred are nonwoven textile materials and especially carpets.

Numerous end use articles can be named for the treated fabrics or products made from the treated materials. Examples include but are not limited to carpets and rags, pillow cases, bed linings, bed sheets, matrices and matrices ticking, curtains, duvet and duvet cases, uphosteries, socks and garments.

Furthermore, the present invention is directed to a method of use for the treatment of polyacrylonitrile fibres to improve the antifungal and/or antidustmite properties, comprising applying to said fibres in the gel state a compound of formula



(1).

Gel state of the polyacrylonitrile fibres is to be understood as the swollen state shortly after preparation of the fibres (freshly spun fibres; typically after removal of the bulk of the non-aqueous spinning solvent used for the preparation of the fibres). A description thereof is given in US-A-4,563,191.

Such a treatment can be carried out according to conventional processes. For example, the polyacrylonitrile fibres are treated in an aqueous liquor containing 0.001% to 10% by weight, especially 0.01% to 5% by weight, based on the weight of the aqueous liquor. An amount of compound of formula (1) of 0.01 to 1% by weight is preferred. Preferably, the treatment is carried out at a temperature of 20 to 100°C, especially 40 to 80°C. For the treatment a pH of the aqueous liquor of 3 to 6 is preferred. If desired, the fibres can be pressed after the treatment to achieve a specified liquid pick-up rate of, for example, 50% to 300%, especially 100% to 300%. Subsequently a heat treatment can be carried out, according to which the treated fibres are dried at temperatures like 60 to 200°C, especially 90 to 200°C.

The above treatment can also be carried out during a dyeing process of these fibres. In such a case the usual dyeing processes for dyeing of these fibres in the gel state apply. Dyes to be used comprise basic dyes. The dyes are then present in the aqueous liquor used for the treatment.

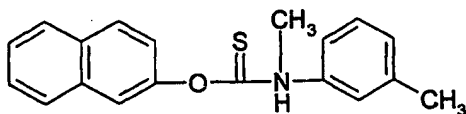
The treatment with the compound of formula (1) can also be carried out together with other chemical agents that would impart the fibres with various desirable to provide various functionality. It is preferred to carry out the treatment in presence of the compound of formula (1) together with an antimicrobial agent, especially antimicrobial substances that exhibit good activities in inhibiting the growth of bacteria, including gram positive and gram negative bacteria.

For all of the above applications of the compound of formula (1) a method of use to improve the antifungal properties is preferred. Likewise, a method of use to improve the antidustmite properties is preferred. Highly preferred is a method of use to improve the antinungal and antidustmite properties.

In the following Examples, percentages are by weight.

Example 1: Preparation of formulation 1

35 g of Tolnaftat (2-naphtyl-N-methy-N-(3-tolyl) thionocarbamate, Cas No. 2398-96-1), 105 g of naphthalenefulfonic acid/formaldehyde condensation product and 560 ml water are mixed in a suitable vessel into which 1000 g of quartz sand has been previously added. The mixture is then homogenized on a tumbling machine for 24 hours. The quartz sand is then filtered off and the resulting formulation 1 contains 5% of Tolnaftat. The median particle size of Tolnaftat in this formulation is measured at about 2 μm with a specific surface area of 3.73 m^2/g .



(Molecular structure of Tolnaftat)

Example 2: Incorporation of the formulation 1

10 g of formulation 1 is added into 500 ml of water. Knitted fabrics made of 100% cotton fibres are impregnated into the bath followed by being pressed with a Lab Padding Machine (Mathias) to give a liquid pick-up rate of 80% o.w.f (on the weight fabric). The resulting fabrics are then dried in an fun assisted oven at 120°C for 5 minutes.

Example 3: Incorporation of the formulation 1

10 g of formulation 1 is added, together with 40 g of Dicylan AS (a product that can form thin films on fabrics, available from Ciba Specialty Chemicals Inc., Switzerland), into 450 ml of water. Knitted fabrics made of 100% cotton fibres are impregnated into the bath followed by being pressed with a Lab Padding Machine (Mathias) to give a liquid pick-up rate of 80% o.w.f (on the weight fabric). The resulting fabrics are then dried in a fun assisted oven at 120°C for 5 minutes

Example 4: Incorporation of formulation 1

10 g of formulation 1 is added into 500 ml of water. Woven fabrics made of 100% wool fibres are impregnated into the bath followed by being pressed with a Lab Padding Machine (Mathias) to give a liquid pick-up rate of 80% o.w.f (on the weight fabric). The resulting fabrics are then dried in a fun assisted oven at 120°C for 5 minutes.

Example 5: Incorporation of formulation 1

Formulation 1 is diluted with water at a ratio of 1:1 (weight/weight). The diluted formulation is then sprayed onto woven fabrics made of 100% of wool fibres with an incorporation level of 2% on the weight of fabrics at room temperature. The treated fabrics are allowed to dry at 70°C in an oven for 10 minutes.

Example 6: Preparation of formulation 2 (comparative example)

10 g of 2,4-dichlorobenzyl alcohol is dissolved into 87 g of 1,2-propylene glycol followed by addition of 3 g of an anionic surfactant sodium lauryl sulphate. The resulting formulation is a clear solution. Upon further diluting with water, the formulation gives a milky dispersion.

Example 7: Incorporation of formulation 2 (comparative example)

200 g of formulation 2 is further diluted with 800 ml of water to produce a dispersion. Cotton fabrics are padded with this dispersion at a pick-up rate of 100%. The padded fabrics are further dried in a fun-assisted oven at 70°C.

Example 8: Preparation of formulation 3 (comparative example)

10 g of a-(2-(4-chlorophenyl)ethyl)-a-(1,1-dimethylethyl)-1H-1,2,4-triazol-1-ethanol

(CAS No. 107534-96-3) is added into 30 g of 1,2-propylene glycol and 60 gram of Marlipol 24/99 (a nonionic surfactant). The resulting product is marked as formulation 3.

Example 9: Incorporation of formulation 3 (comparative example)

20 g of formulation 3 is added into 1000 ml of water. Knitted fabrics made of 100% cotton fibres are padded with a Mathias Lab padding machine with a pick-up rate of 80-100%. Padded fabrics are further dried in a fun-assisted oven at 120°C for 5 minutes.

Example 10: Incorporation of formulation 1

In this example freshly spun and wet (moisture content ca. 170%) polyacrylonitrile fibres are treated. A treatment bath is prepared and it consists of the following:

50 gram of formulation 1

50 gram of Tinosan AM 100 (antimicrobial agent, available from Ciba Specialty Chemicals Inc., Switzerland)

Add water to 1000 ml

pH of the treatment bath is adjusted to 4.5

The treatment bath is heated to 55-60°C, freshly spun and wet polyacrylonitrile fibres are dipped into the bath and allowed to remain for about 5 seconds, the treated fibres are then pressed with a Lab padding machine to achieve total wet pick-up rate of about 200%. The treated and wet fibres are then dried in an oven at 160°C for 15 minutes.

Example 11: Washing of fabrics and fibres

The treated fabrics and/or fibres are occasionally washed in a conventional laundering process to examine the washing durability of antibacterial and/or antifungal activities imparted by various treatment with various agents. Unless otherwise stated, the washing conditions are as follows:

Washing conditions: according to a standard (BS 4923 4A standard)

Detergent: Persil, 2.25% owf

Washing machine: Wascator FOM 71MP

Temperature: 50 ± 3°C

Cycle time: 50 minutes
Liquor ratio: 1:10
Rinsing: 4 cycles, room temperature
Agitation: gentle
Drying: tumble dryer

Samples are washed for various cycles such as 5, 10 and 20.

Example 12: Microbiological activities of fabrics treated with Formulation 1

a) Method Principle

Discs of fabrics with a diameter of 2 cm were punched from the samples.

The discs were applied on the top layer of solidified agar containing the fungal suspension (5 ml of a washed agar slant were added to 500 ml molten agar and 5-6 ml were distributed on the bottom layer).

All plates were then put at 28°C. After incubation the zones of inhibition around the samples (20 mm discs) were measured, the growth under the discs evaluated (Vinson rating) and reported in the following Table 1.

Fungi: Aspergillus niger ATCC 6275
Medium: Sabouraud agar + 4% glucose (two layers of agar: 15 ml bottom layer without germs and 6 ml top layer containing the mould)
Incubation: 5 days at 28°C

b) Table 1

Tested fabric samples:	Test strain: Aspergillus niger ATCC 6275	
	ZI	VR
Cotton placebo	0 / 0	0 / 0
Cotton treated as illustrated in Example 2	5 / 5	4 / 4
Cotton treated as illustrated in Example 2 20 times washed	3 / 3	4 / 4
Cotton treated as illustrated in Example 3	5 / 5	4 / 4
Cotton treated as illustrated in Example 3 20 times washed	3 / 4	4 / 4
Wool placebo	0 / 0	0 / 0
Wool treated as illustrated in Example 4	6 / 6	4 / 4
Wool treated as illustrated in Example 4 3 times dry cleaned with commercial launder	3 / 3	4 / 4
Wool treated as illustrated in Example 5	6 / 6	4 / 4

All tests were performed twice and both results are given in the above table.

Legend: ZI = zone of inhibition in mm

VR = Vinson rating, for growth under the disc.

(L.J. Vinson et al. J.Pharm. Sci. 50, 827-830, 1961)

0 = strong growth under the disc (no activity)

4 = no growth under the disc (good activity)

Example 13: Microbiological activities of fabrics treated with formulation 1

Polyacrylonitril fibres made as described in Example 10 were also tested for antimicrobial performances. In addition to fungal strains, representative bacteria (gram positive and gram negative) were also chosen for tests. The incubation time in case of carrying out of the tests relating to bacteria was overnight (18-24 hours). Otherwise the test method was the same as described in example 12. The results as illustrated by the zone of inhibition can be found in the following Table 2.

Table 2

	Samples treated as illustrated in Example 10	
	treated with Formulation 1 and Tinosan AM 100	treated with Formulation 1 only
Microorganisms	Zone of inhibition (mm)	
<i>Aspergillus niger</i> ATCC 6275	2 / 2	2 / 2
<i>Trichophyton Mentagrophytes</i> ATCC 9533	7 / 7	5 / 5
<i>Staphylococcus aureus</i> ATCC 9144	30 / 30	0 / 0
<i>Escherichia coli</i> NCTC 8196	20 / 20	0 / 0

Example 14: Microbiological activities of fabrics treated with Formulation 2

(comparative example)

Antimicrobial performances for the samples treated with formulation 2 was evaluated according to the method described in Example 12. Thus the following results were obtained:

Table 3

	Samples treated as illustrated in Example 7	
	treated with Formulation 2, unwashed	treated with Formulation 2, washed 10 times
Microorganisms	Zone of inhibition (mm)	
<i>Aspergillus niger</i> ATCC 6275	0 / 0	0 / 0
<i>Trichophyton Mentagrophytes</i> ATCC 9533	12 / 12	0 / 0
<i>Staphylococcus aureus</i> ATCC 9144	3 / 3	0 / 0
<i>Escherichia coli</i> NCTC 8196	7 / 7	0 / 0

All tests were performed twice and both results are given in the table

Example 15: Microbiological activities of fabrics treated with Formulation 3**(comparative example)**

The tests were carried out according to the method described in Example 12.

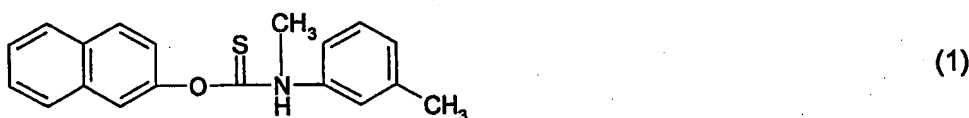
Table 4

Tested fabric samples (Samples treated as illustrated in Example 9)	Microorganism: Aspergillus niger ATCC 6275		Microorganism: Tr. Mentagrophytes ATCC 9533	
	Z	VR	Z	VR
Treated with 10 g/l formulation 3, unwashed	1 / 1	4 / 4	5 / 5	4 / 4
Treated with 10 g/l formulation 3, washed 20 times	0 / 0	0 / 0	0 / 0	0 / 0
Treated with 20 g/l formulation 3, unwashed	3 / 3	4 / 4	8 / 8	4 / 4
Treated with 20 g/l formulation 3, washed 20 times	0 / 0	0 / 0	0 / 0	0 / 0

All tests were performed twice and both results are given in the table

Claims

1. A method of use for the treatment of textile material to improve the antifungal and/or antidustmite properties, comprising
applying to the textile material a compound of formula



by padding, spraying, foam application or during a dry cleaning process.

2. A method of use according to claim 1, wherein the compound of formula (1) is applied to the textile material together with dyestuffs in a dyeing process carried out padding, spraying or foam application.
3. A method of use according to claim 1, wherein the compound of formula (1) is applied to the textile material in a finishing process carried out by padding, spraying or foam application.
4. A method of use according to any of claims 1 to 3, wherein the compound of formula (1) is applied to the textile material as aqueous formulation in diluted, solubilised, emulsified or dispersed form.
5. A method of use according to any of claims 1 to 4, wherein the compound of formula (1) is dispersed with at least one dispersant selected from the group consisting of acid esters or their salts of alkylene oxide adducts; polystyrene sulfonates; fatty acid taurides; alkylated diphenyl oxide mono- or disulfonates; sulfonates of polycarboxylates; the polyadducts of 1 to 60 mol of ethylene oxide and/or propylene oxide with fatty amines, fatty acids or fatty alcohols, each containing 8 to 22 carbon atoms in the alkyl chain, with alkylphenols containing 4 to 16 carbon atoms in the alkyl chain, or with trihydric to hexahydric alkanols containing 3 to 6 carbon atoms, which polyadducts are converted into an acid ester with an organic dicarboxylic acid or with an inorganic polybasic acid; ligninsulfonates; and formaldehyde condensates.

6. A method of use according to any of claims 1 to 5, wherein the compound of formula (1) is dispersed with at least one dispersant selected from the group consisting of condensates of ligninsulfonates and/or phenol and formaldehyde; condensates of formaldehyde with aromatic sulfonic acids; condensates of naphthalenesulfonic acid and/or naphthol- or naphthylaminesulfonic acids with formaldehyde; condensates of phenolsulfonic acids and/or sulfonated dihydroxydiphenylsulfone and phenols or cresols with formaldehyde and/or urea; and condensates of diphenyl oxide-disulfonic acid derivatives with formaldehyde.

7. A method of use according to any of claims 1 to 6, wherein the compound of formula (1) is applied to the textile material by padding and wherein said textile material is continuously passed through an aqueous liquor containing 0.001% to 10% by weight, based on the weight of the aqueous liquor, of the compound of formula (1).

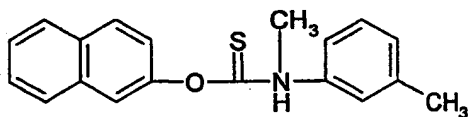
8. A method of use according to any of claims 1 to 6, wherein the compound of formula (1) is applied to the textile material by spraying, wherein an aqueous liquor containing 0.001% to 10% by weight, based on the weight of the aqueous liquor, of the compound of formula (1) is sprayed onto the textile material.

9. A method of use according to any of claims 1 to 6, wherein the compound of formula (1) is applied to the textile material by foam application, wherein an aqueous foam containing 0.001% to 10% by weight, based on the weight of the aqueous foam, of a compound of formula (1) and optionally a foam stabiliser is applied to the textile material.

10. A method of use according to any of claims 1 and 4 to 6, wherein the compound of formula (1) is applied to the textile material during a dry cleaning process, wherein the textile material is treated with an organic solvent, preferably perchloroethylene or trichloroethylene, containing 0.001% to 10% by weight, based on the weight of the organic solvent, of a compound of formula (1).

11. A method of use according to any of claims 1 to 10, wherein the textile material is selected from natural or synthetic polyamide, polyurethane, polyester, polypropylene, polyethylene, polyacrylonitrile and cellulose-containing textile materials.

12. A method of use according to any of claims 1 to 11, wherein the textile material is selected from wool, synthetic polyamide, polyester, polypropylene, polyethylene and cellulose-containing textile materials, preferably cotton or wool.
13. A method of use according to any of claims 1 to 12, wherein the textile material is a nonwoven textile material or a carpet, preferably a carpet.
14. A method of use for the treatment of polyacrylonitrile fibres to improve the antifungal and/or antidustmite properties, comprising applying to said fibres in the gel state a compound of formula



(1).

15. A method of use according to any of claims 1 to 14 to improve the antifungal properties.
16. A method of use according to any of claims 1 to 14 to improve the antidustmite properties.

INTERNATIONAL SEARCH REPORT

Int. Application No.

PCT/EP 01/08662

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 D06M13/425 D06M23/04 D06L1/04 D01F11/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D06M D06L D01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 937 812 A (CIBA GEIGY AG) 25 August 1999 (1999-08-25) page 5, line 57 -page 9, line 18 claims 1,13,22,23 ---	1-9, 11-13, 15,16
X	DE 23 38 633 A (SCHNEIDER PETER DR MED) 20 February 1975 (1975-02-20) page 3, line 9 - line 15 example 1 claims ---	1,3-7, 11-13, 15,16
Y	WO 98 36111 A (BRIGGS NIGEL PHILIP ;COURTAULDS PLC (GB)) 20 August 1998 (1998-08-20) page 3, line 1 - line 22 example 2 ---	14-16
	--- -/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

4 December 2001

Date of mailing of the international search report

19/12/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Fiocco, M

INTERNATIONAL SEARCH REPORT

Int. Patent Application No

PCT/EP 01/08662

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 746 959 A (TAYLOR JONATHAN MICHAEL ET AL) 5 May 1998 (1998-05-05) abstract -----	14-16
Y	EP 0 488 294 A (MITSUBISHI RAYON CO) 3 June 1992 (1992-06-03) page 5, line 45 - line 58 -----	14-16
A	US 3 625 644 A (NOSLER HEINZ GUNTER ET AL) 7 December 1971 (1971-12-07) abstract -----	10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/08662

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0937812	A	25-08-1999	EP 0937812 A2	25-08-1999
DE 2338633	A	20-02-1975	DE 2338633 A1	20-02-1975
WO 9836111	A	20-08-1998	AU 6000798 A	08-09-1998
			WO 9836111 A1	20-08-1998
			ZA 9801138 A	20-08-1998
US 5746959	A	05-05-1998	GB 2309461 A , B	30-07-1997
EP 0488294	A	03-06-1992	JP 2952613 B2	27-09-1999
			JP 4245978 A	02-09-1992
			JP 4202854 A	23-07-1992
			EP 0488294 A2	03-06-1992
			US 5238682 A	24-08-1993
US 3625644	A	07-12-1971	DE 1812054 A1	18-06-1970
			AT 300727 B	15-07-1972
			BE 742383 A	28-05-1970
			CH 525324 A	15-07-1972
			DK 122575 B	20-03-1972
			FR 2033201 A5	04-12-1970
			NL 6916604 A	04-06-1970

THIS PAGE BLANK (USPTO)